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Measuring Metal Sulfide Complexes in Oxic River Waters with Square Wave Voltammetry

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A sulfide identification protocol was developed to quantify specific metal sulfides that could exist in river water. Using a series of acid additions, nitrogen purges, and voltammetric analyses, metal sulfides were identified and semiquantified in three specific groups: (a) Co, Fe, Mn, and Ni (bi)sulfides, (b) Fe, Zn, and Pb sulfides, and (c) Cu sulfides. All metal sulfide complexes were measured in low nanomolar concentrations in the oxic waters of four Connecticut rivers, using a thin mercury film rotating disk glassy carbon electrode (TMF-RDGCE). The short residence times associated with a RDE prevents certain strong metal sulfide complexes (Cu, Zn, and Pb) from dissociating at pH > 7.0 during depositions, which allows for identification in certain pH zones. The concentrations of the specific metal sulfide complexes were linked to the extent of watershed development and proximity to source areas. At sampling sites impacted by treated sewage effluent, the concentrations of Cu and Zn sulfide complexes accounted for over 30% of the total metals passing through a 0.45-μm filter. Ultrafiltration revealed that between 30% and 60% of these Cu and Zn sulfide complexes were >3000 MW and probably associated with organic matter. A kinetic loss experiment showed that the Cu and Zn sulfide complexes had half-lives > 15 days, demonstrating the importance of these complexes as metal carrier in small- and medium-sized river systems.

Introduction

Determining speciation is fundamental to understanding the behavior of trace metals in freshwater environments. Since most of these waters are oxygenated, the role of sulfides has received little attention in the freshwater literature. However, sulfides in nanomolar and picomolar concentrations have been observed in the open ocean (*1*−*4*). The persistence of the sulfides in these oxic waters is thought to be due to the formation of relatively stable metal sulfide complexes (*1*−*4*). In rivers, potential source environments, such as headwater marshes, dam sediments, and sewage treatment plants, exist where trace metal and sulfide concentrations could exceed the metal sulfide solubility products resulting in the formation of metal sulfide complexes. As in seawater, the large binding constants could allow for the persistence of metal sulfide complexes in downstream waters.

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Several recent laboratory studies have been conducted using square wave voltammetry with hanging drop mercury electrodes to determine both the proton stoichiometry and the conditional stability constants of metal sulfides in seawater. These methods include (i) measuring the stripping current of deposited sulfide species during titration of bisulfides with metal ions (*5*), (ii) measuring free bisulfide and free metal ions (using competitive ligand exchange with oxine) during independent titrations of bisulfide with metals (*6*, *7*), and (iii) measuring potential shifts and currents of bisulfides during titrations with metals (*7*). All of these studies have found similar conditional stability constants for most of the divalent metal (bi)sulfide (1:1) complexes (*6*, *7*), which would allow, at least theoretically, for the existence of these species in oxic waters.

Luther et al. (1996) investigated the stoichiometries of metal sulfide complexes by monitoring both potential and current during acid−base titrations following metal sulfide formation. By using an acid titration, several interesting observations were made. First, it was noted that by decreasing the pH the sulfide peak shifted to a more positive potential. This was a result of the electrochemical reversibility of the bisulfide oxidation of the Hg at the surface of the hanging drop (eq 1). This allows the reaction to be expressed in a Nernstian form (eq 2):

$$HS^- + Hg \rightarrow HgS + H^+ + 2e^- \quad (1)$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[HS^-]}{[H^+]} \quad (2)$$

Equation 2 clearly shows that the potential shift is linked to the pH.

The second important finding showed that dissociation of specific metal sulfides was pH-dependent. Co^{2+}, Fe^{2+}, Mn^{2+}, and Ni^{2+} were shown to form bisulfide complexes, which dissociated while purging with N_2. Zn sulfides were observed to dissociate at pH < 6.7, whereas Cu sulfides did not begin to dissociate until pH < 5.0. In fact, the Cu complexes were not fully dissociated even at pH < 2.0. This was attributed to the reduction of Cu(II) to Cu(I) by the sulfides during complexation. Interestingly, the sulfide peak from the Cu sulfide dissociation was slightly more negative than the sulfide peak from the Zn complexes, which undergo dissociation with a release of H_2S (pH < 7) in a manner similar to Co, Fe, Mn, and Ni. At pH < 5, the negative shift in the sulfide peak was thought to be due to the measurement of a singularly protonated Cu sulfide complex versus H_3S^+ that would form from dissociated sulfides.

While this work provoked some controversy with respect to the determination of stability constants (*8*, *9*), it presented a potential method for identifying and semiquantifying metal sulfide species in natural waters by electrochemically measuring sulfide at different pH values. The term semiquantification is used in this research since the exact stoichiometries of the Zn and Cu sulfides in natural samples would not be known.

Cathodic stripping square wave voltammetry (CSSWV) was conducted using a thin mercury film rotating disk glassy carbon electrode (TMF-RDGCE) to increase the sensitivity needed to identity and quantify metal sulfide complexes at real world concentrations. The high rotation rate of RDE has the added benefit of reducing residence times of any diffusing species at the electrode surface, since the diffusion layer thickness is proportional to $1/(\omega)^{-1}$ (*10*). The small residence times (ca. 20 ms for a 4000 rpm rotation) minimized any

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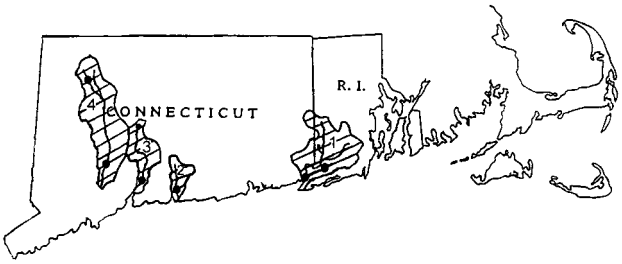

1 Pawcatuck Watershed
2 Hammonasset Watershed
3 Quinnipiac Watershed
4 Naugatuck Watershed

● Sampling Locations

FIGURE 1. Sampling locations in Connecticut.

potential Hg−Me substitution reactions from occurring while the inert metal sulfide complexes of Cu, Zn, and Pb were in the diffusion layer. Thus, sulfides would not be measured at the electrode for these complexes, until the complexes dissociated on acid addition (*11*).

Our research was designed to test the applicability of CSSWV and acid−base titrations in the laboratory and then use this procedure to identify and semiquantify any metal sulfide species persisting in oxic river water. Laboratory experiments were conducted (1) to validate the use of the TMF-RDGCE, (2) to ensure Fe, Zn, and Cu sulfides could be identified in a multimetal solution, (3) to identify the stoichiometry of Pb sulfide species, and (4) to estimate the percent dissolution of Cu sulfides at low pH though Cu(I) measurements. Field samples were collected in February and May to determine if metal sulfide complexes persist in oxic river waters in both winter and early summer. Using parallel trace metal measurements (Cu, Fe, Mn, Pb, and Zn), the percentage of metals bound to sulfides could be estimated. These methods were augmented by the use of ultrafiltration (3000 MW cutoff) to begin to understand the size fractionation of these complexes.

Field Sites. Sampling locations were selected to cover a wide range of biogeochemical regimes and levels of watershed development in southern New England (Figure 1, Table 1). On three rivers, two sites were selected to begin to study the effect of watershed development on one individual river system. Two of the developed watersheds, the Naugatuck and Quinnipiac Rivers, had sewage treatment plants (STP) located between the upstream and downstream sampling sites. This would allow us to see the effect of STP effluent on metal sulfide concentrations in the rivers.

Methods

Voltammetry was performed using either a EG&G 384 polarographic analyzer, Bioanalytical Systems (BAS) CV50W, or an Analytical Instruments Systems (AIS) DLK-100 with a ROTEL rotating disk electrode (Ag^+/AgCl double junction reference electrode). Voltammetric measurement techniques were independent of the analyzer used. The square wave stripping parameters used were 200-mV/s scan rate with a 24-mV pulse height. The direction of the potential that was scanned during laboratory experiments was dependent on whether metals (anodic) or sulfides (cathodic) were being measured but ranged from −0.1 to −1.4 V. To increase the sensitivity for field samples a 60-s deposition at −0.1 V was used. All depositions were conducted at a rotation rate of 4000 rpm.

Standard solutions were made using ACS reagent grade $Na_2S{\cdot}9H_2O$ and ACS grade metal salts (Aldrich). All solutions were prepared with Nanopure water (Barnstead) that had been purged with N_2 for 1 h. All samples were then maintained under a N_2 blanket. N_2 was first passed through a pyrocatechol trap, lowering O_2 concentrations < 0.2 μM. Acid titrations were conducted using ultrapure 0.01 N HNO_3 (Seastar), and pH was monitored using a solid-state electrode (Orion). To increase current response, ionic strengths of laboratory and field samples were increased to 0.01 M KCl (Sigma, specpure grade), the exception was for laboratory Cu(I) standardization, which was measured at an ionic strength of 0.01 M HNO_3.

TABLE 1. Background Water Chemistries from the Rivers During the February and May Sampling Dates[a]

river	pH	dissolved oxygen (mg/L)	alkalinity (μequiv/L)
Hammonasset			
low development			
2/97	6.6	18	100
5/97	6.8	13	130
Pawcatuck			
headwaters			
2/97	5.1	19	60
5/97	5.6	16	72
medium development			
2/97	6.1	18	180
5/97	6.6	15	205
Quinnipiac			
headwaters			
2/97	7.4	20	1200
5/97	7.9	14	1450
high development			
2/97	7.3	18	1180
5/97	7.5	12	1300
Naugatuck			
headwaters			
2/97	6.9	22	250
5/97	7.2	15	273
high development			
2/97	7.1	20	380
5/97	7.9	13	440

[a] Values in parentheses represent concentrations in the truly dissolved fractions.

All sample preparation, collection, and analysis were conducted using clean techniques (*12*). Samples were filtered (0.45 μm) in the field and immediately packed in ice for transport. All subsequent laboratory manipulations were performed in a Class 100 clean room. Sulfide measurements were made within 3 h (conventional filtrate) or 4 h (ultrafiltrate) of collection.

Even though laboratory analysis was conducted a maximum of 3 h after collection, the possibility of oxidation and/or exchange between the different metals existed. To determine if any sulfide was oxidized during transport, sulfides were immobilized in separate river samples using zinc acetate at pH = 10. Upon return to the laboratory, nonimmobilized water and immobilized river water were both measured by the Cline method for total sulfide. A 50× preconcentration step was used to increase sensitivity to low micromolar levels. Following this step, the $Zn(OH)_2$−ZnS floc was redissolved in a volume of acid that was smaller than the original sample volume. The nonimmobilized sample averaged 93 ± 5% of the immobilized sample.

Ultrafiltrations were performed immediately upon returning to the laboratory, allowing for complete size fractionation and sulfide analysis to be completed within 4 h of collection. Ultrafiltration was performed with a H1P30 hollow fiber cartridge (Amicon) with a 3000 MW cutoff. Concentration factors were typically 6×, and pump pressures were <15 psig. Sulfide measurements were conducted immediately following the ultrafiltration.

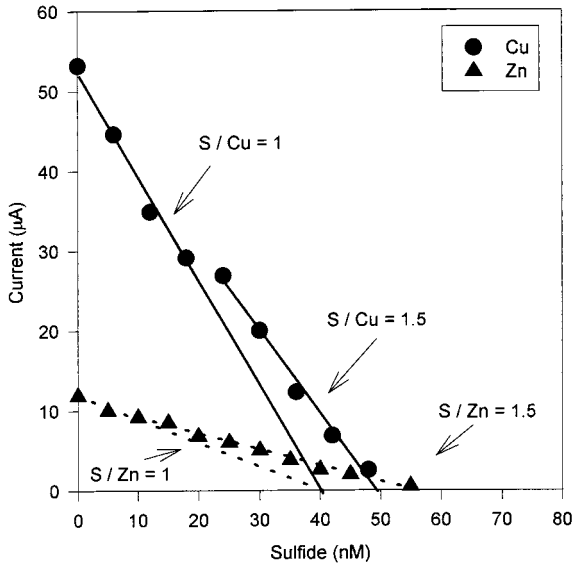

FIGURE 2. Current versus sulfide concentration plots for separate titrations of 40 nM Cu and 40 nM Zn with sulfide in 0.01 KCl and 1 mM $NaHCO_3$ buffer.

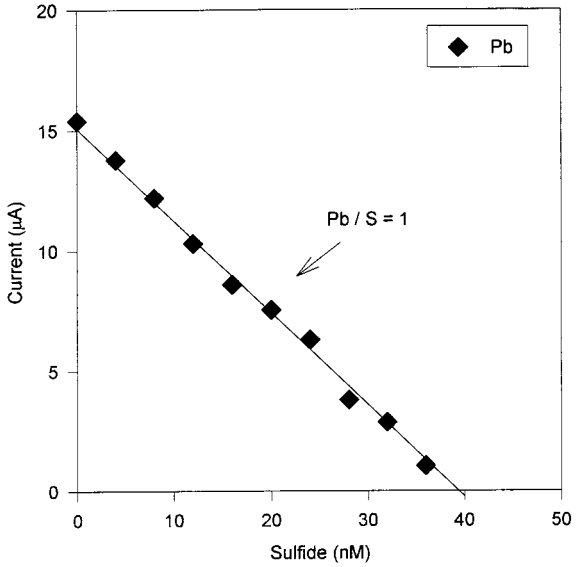

FIGURE 3. Current versus sulfide concentration plots for the titrations of 40 nM Pb with sulfide in 0.01 KCl and 1 mM $NaHCO_3$ buffer.

Results and Discussion

Metal Sulfide Identification Curves. Before field measurements were conducted, sulfide titrations were conducted on laboratory-prepared samples of Cu, Zn, or Pb. These titrations were performed at nanomolar levels to reflect possible natural levels; however, even at these concentrations the metal sulfide solubility constants were still exceeded in the solutions where pH = 7.2. This oversaturation is necessary to promote multinuclear complexation (*7*). The resulting metal:sulfide stoichiometries using TMF-RDGCE were similar to those of Luther et al. (*7*), with both 1:1 and 2:3 ratios of metal:sulfide being seen for Zn and Cu (Figure 2). The new Pb data, however, only showed 1:1 complexation (Figure 3). In all cases no excess sulfide was detected when free metals were present.

Solutions consisting of Fe, Zn, and Cu metal sulfides were added together and then acid-titrated to determine if sulfides from individual metal sulfide complexes could be recovered. At pH = 6.7, Fe (bi)sulfides had sulfide mass recoveries of over 93%. At pH = 6.0, the increase in the sulfide peak accounted for 85% of the sulfide used in the Zn sulfide complexation. A final acidification to pH = 2.8 resulted in only a 68% Cu sulfide complex recovery, even after a 10-min equilibration period.

To provide an additional check on sulfide recovery from the Cu sulfide complexes, Cu(I) was measured in separate acidified samples of laboratory-prepared Cu sulfide complexes. The Cu sulfide complexes were formed by titrating 100 nM Cu^{2+} solutions with 20 nM aliquots of HS^- at pH = 8.0. Cu was monitored, and the sulfide titration ended when no detectable Cu was present. The solutions were then acidified to pH = 2 by the addition of HNO_3. No chlorides were added for ionic strength adjustment, which allowed for the voltammetric scans at potentials greater than 0.0 V. Anodic scans were then performed over a potential range of −0.4 to 0.15 V (eqs 4−6) to measure any free Cu. The resulting scans

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad -0.15\ V \qquad (3)$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad -0.33\ V \qquad (4)$$

$$Cu^+ + e^- \rightarrow Cu \qquad 0.05\ V \qquad (5)$$

showed only one peak at 0.05 V, indicating all the free Cu had been reduced to Cu(I). After the procedural 10-min equilibration period 73% of the total Cu added was recovered, which matched with our estimate from S(0) measurements. This gave us additional confidence that a semiquantification of natural Cu sulfides was possible.

Competition between Metals. Since natural samples presumably have a mixture of metal sulfide complexes, laboratory experiments were performed to see the effects of acid titrations on solutions containing two or more metal sulfide species. The major concern was that when metal sulfides dissociated at low pH the free sulfides would then be available to react with other metals. To test for this potential problem, a solution containing 40 nM Zn was titrated with HS^- at pH = 8.0 until no detectable Zn was present; 40 nM Cu was then added, and the solution was acidified to a pH of 6.5. A cathodic scan following a 60-s deposition period at −0.1 V failed to detect any free sulfide, indicating the sulfides liberated by acidification had become bound to the Cu. However, in natural systems very little free Cu is present. Xue and Sunda (*13*) used competitive ligand exchange−cathodic stripping voltammetry to measure free Cu in lake water, where they found the concentration of free Cu to average 10^{-14} M. In the same river water we sampled for metal sulfides, differential pulse anodic stripping voltammetry showed that free Cu concentrations were at 10^{-10} M levels (*14*). In both cases, the most probable ligand, acting to lower free Cu levels, is dissolved organic matter.

To simulate more natural conditions, a second experiment was performed using a solution containing an equimolar amount of a Cu humic complex and Zn sulfide complexes. To accomplish this, 20 nM Cu was added to a solution containing 1 mg of C/L of humic acid adjusted to pH = 8. Following a 15-min equilibration period, the solution was anodically scanned, after a 120-s deposition at −0.7 V. No free Cu was observed, indicating all the Cu was bound to the humics. Titrated Zn sulfide complexes (40 nM) were added to the solution. Again, the solution was adjusted to pH = 6.5 and cathodically scanned following a 60-s deposition at −0.1 V. In this case, a sulfide peak was observed along the free sulfide acid/base titration curve, with 87% of the sulfides being recovered.

Metal Sulfide Identification. On the basis of pH, sulfide release from the dissociation of specific metal sulfide complexes could be grouped into three distinct pH zones (Table 2). In each zone, sulfides could be electrochemically measured and then removed (as H_2S) by a N_2 purge. Solutions could then be titrated with acid and the pH lowered to the next

TABLE 2. Potential Sources to Sulfide Peak at Different pH Levels

group	pH	species
I	>6.7	metal (bi)sulfides of Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, free sulfide, polysulfides, elemental sulfur
II	5.0−6.7	metal sulfides of Zn^{2+}, Pb^{2+}, Cd^{2+}, and FeS
III	<5.0	metal sulfides of Cu^{2+}

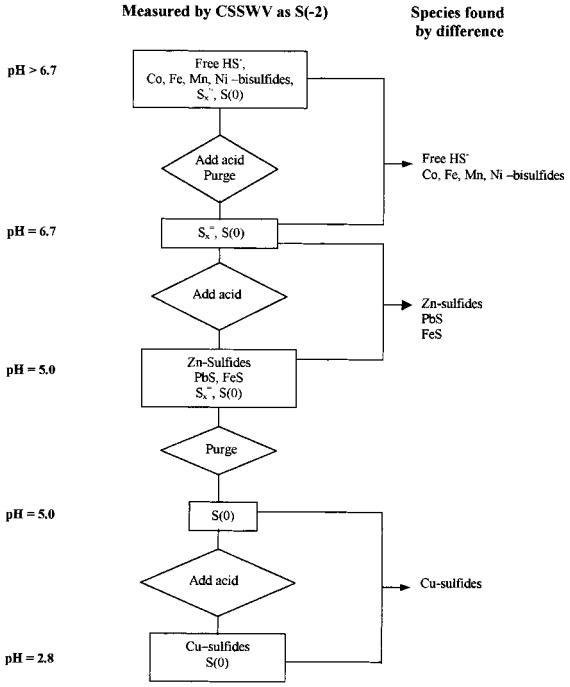

FIGURE 4. Sulfide identification protocol.

zone. This simplistic acid titration combined with a follow-on N_2 purge would allow for the isolation of the specific metal sulfides as measured by Luther et al. (1976). However in natural systems other metal sulfides and free sulfur could complicate this approach. At pH levels typically found in river water (pH > 6.7), any free sulfide, polysulfides, and elemental sulfur present could also add to the sulfide signal being measured (*15, 16*). Additionally, other trace metals have the possibility to form metal sulfide complexes, which in turn would dissociate during acid titrations and release sulfides.

To account for the complexity found in natural waters, the additional sources of sulfide in each pH zone would have to be accounted for. Added to Co, Fe, Mn, and Ni (bi)sulfides were free sulfide, polysulfides, and elemental sulfur. Several other important trace metals, Pb^{2+}, Cd^{2+}, and Ag^{+}, were included with Zn sulfide complexes, though only Pb sulfides were expected to be in significant quantities to affect the sulfide peak. These metals were grouped together based on the assumption that no metal reduction occurred during the sulfide complexation, as in the case of Zn sulfide complexation. Soluble FeS was also included with the MS complexes (*17*).

Identification Protocol. To minimize interferences from free sulfur species and semiquantify specific metal sulfide complexes in natural waters, we developed a protocol consisting of a series of acid additions and N_2 purges (Figure 4). The first step was to measure free sulfides and labile Co, Fe, Mn, and Ni (bi)sulfides. This could simply be accomplished by measuring the initial sulfide peak in the oxic waters and the resulting sulfide peak after acidifying the samples to pH = 6.8 and conducting a 10-min N_2 purge. A stabilized sulfide peak (after repeated scans) would indicate all free sulfides and Co, Fe, Mn, and Ni (bi)sulfides had been removed. Quantification could be achieved by difference. The resulting sulfide peak, if present, would be composed of only free polysulfides and elemental sulfur, since Zn, Cu, or Pb sulfide complexes would not have begun to dissociate. Next, the pH would be lowered to pH = 5.2, allowed to equilibrate for 30 s without purging, and analyzed. Additional equilibration periods (typically 2−3) were conducted until a maximum sulfide peak was observed. At this pH, the sulfide peak (originally from S(0) and S_x^{2-}) should increase from the dissociation of Zn and Pb sulfide complexes and any soluble FeS. Again, the total sulfide from metal complexation could be found by difference. Although, FeS has been identified with its own discrete peak at −1.1 (*17*), FeS only forms when the IAP > K_{sp}. At nanomolar levels found in natural systems, the $IAP_{FeS} < K_{spFeS}$, so significant amounts of FeS were not expected in the rivers. Unfortunately, we did not measure the FeS signal discretely and were not able to confirm this during our study. We were able to determine if S(0) was present, by purging at pH = 5.2 and measuring the sulfide peak. The remaining sulfide peak would now be composed of S(0) from either free S(0) and/or S(0) that had been produced from the breakdown of polysulfides, which occurs at pH < 6.5 for S_4^{2-} and pH < 6.1 for S_5^{2-} (*16*, *18*). The other breakdown product of polysulfides is HS^-, which could cause an overestimation in the amount of Zn and Pb sulfide complexes present. However, none of our samples had any sulfide peak after a 5-min purge at pH = 5.2, indicating no S(0) or S_x^{2-} was present. Finally, the pH was lowered to pH = 2.8. In the idealized case, the sulfide peak now would be composed of entirely S(−2) from either Cu sulfide dissociation and/or the S(0) from the previous pH. A second peak slightly more negative could also occur, representing the protonated Cu sulfide complex. Measurements would be repeated after a 10-min equilibration with peak growth being attributed to Cu sulfide dissociation. H_2S loss was minimized at these levels by using a N_2 blanket.

In river waters, the ambient pH is not always above pH = 6.8. In river waters with ambient pH < 6.8, voltammetric measurements were taken before and after an initial purge for 10 min. Any change in the peak sulfides was assumed to be from just Co, Fe, Mn, and Ni (bi)sulfides. The protocol was then used as before. If the river water had pH < 5.2, the change in the sulfide peak from the initial purge was estimated to be from residual Zn sulfide complexes.

Metal Sulfides in River Water. Our field sampling indicates that total dissolved sulfides are commonly present in low nanomolar quantities in oxic surface waters. Table 3 shows total sulfide levels from both sampling dates in February and May 1997. The sulfide concentration was determined for group I, represented by MSH^+, group II represented by ΣZn-S, and group III, represented by ΣCu-S. No free sulfides were measured in any samples, indicating that metal sulfide complexes were responsible for the persistence of sulfides in oxic waters.

The abundance of specific metal sulfide complexes varied from site to site and appeared to be linked to the ambient conditions (including time of year) and the extent of watershed development. The majority of the sulfide complexes were due to Cu and Zn, even though, in the waters tested, Fe > Mn > Zn > S^{2-} > Cu. This is probably a result of stronger binding constants for Cu and Zn (*7*), which prevent oxidation and provided a greater resistance to dissociation in slightly acidic waters.

In fact, in the Pawcatuck River, ambient pH controlled the amounts of metal sulfide. At the headwaters, large cedar swamps lowered the pH < 6.0. This clearly affected the sulfide distribution, with no Co, Fe, Mn, or Ni (bi)sulfides being

TABLE 3. Trace Metal and Sulfide Data for the Four Connecticut Rivers Sampled in February and May 1997[a]

river	MSH^+ (nM)	Cu (nM)	ΣCu-S (nM)	complexed (%)	Zn (nM)	ΣZn-S (nM)	complexed (%)
Hammonasset							
low development							
2/97	<0.5	5.1 (2.1)	1.8 (0.5)	30 (25)	61 (33)	3.5 (1.2)	0.05 (0.03)
5/97	<0.5	5.8 (1.4)	2.1 (0.5)	31 (30)	91 (58)	1.6 (0.5)	0.02 (0.01)
Pawcatuck							
headwaters							
2/97	nd	4.4 (3.1)	3.1 (1.2)	59 (33)	76 (42)	1.8 (<0.5)	0.02 (<0.1)
5/97	nd	5.2 (2.9)	3.4 (1.1)	54 (32)	120 (64)	1.5 (<0.5)	0.01 (<0.1)
medium development							
2/97	<0.5	7.5 (3.0)	4.8 (1.2)	53 (34)	126 (84)	13 (5.2)	8.3 (4.5)
5/97	2.0	8.2 (3.0)	6.0 (1.8)	60 (50)	139 (88)	17 (8.2)	9.7 (7.0)
Quinnipiac							
headwaters							
2/97	7.3	14.3 (8.3)	9.2 (4.2)	54 (42)	101 (64)	15 (5.6)	11 (6.7)
5/97	23.3	20.4 (14)	7.5 (3.6)	31 (22)	122 (79)	9.2 (3.4)	5.6 (3.3)
high development							
2/97	18.1	31.7 (15)	13.3 (2.1)	36 (14)	169 (94)	22 (6.9)	9.7 (7.3)
5/97	30.6	43.4 (19)	15.9 (4.4)	31 (18)	246 (152)	18 (9.2)	5.5 (4.5)
Naugatuck							
headwaters							
2/97	6.1	6.2 (3.0)	1.5 (0.6)	13 (17)	132 (65)	11 (4.8)	6.3 (5.5)
5/97	10.3	5.9 (1.6)	1.7 (<0.5)	24 (<25)	121 (87)	15 (3.7)	9.0 (3.1)
high development							
2/97	15.9	50 (24)	8.2 (1.2)	13 (4)	336 (198)	21 (7.2)	4.7 (2.7)
5/97	23.1	57 (29)	13.7 (7.6)	25 (22)	273 (136)	18 (9.6)	7.6 (7.1)

[a] Numbers in parentheses indicate the truly dissolved fraction (<3000 MW). MSH^+ represents the sulfide measured from all Co, Fe, Mn, and Ni (bi)sulfides. ΣMe-S is the sum of all sulfides from Cu or Zn sulfide complexes. For each river, headwater sites are relatively undeveloped, while either medium (Pawcatuck) or heavy (Naugatuck and Quinnipiac) development characterizes downstream sites. Sewage treatment effluent discharges upstream the Quinnipiac and Naugatuck sites, while septic systems are located in both the Hammonasset and Pawcatuck (downstream site only) watersheds.

measured at our detection limit of 0.5 nM sulfides. Zn sulfide complexes were present but at <2 nM. These complexes were also larger than the 3000 MW cutoff and may be associated with an organic component. At the downstream location with pH > 6.2, the concentration of Zn sulfide complexes increased by an order of magnitude. Some MSH^+ complexes were observed in the summer when pH = 6.6.

The extent of watershed development also played a key role in the amounts of metal sulfides observed in the rivers. A comparison of the downstream sites on the highly developed Naugatuck and Quinnipiac Rivers revealed similar Cu and Zn sulfide complex concentrations of 15 and 20 nM, respectively. The upstream sites on these rivers were much less. In fact, the headwaters of the Naugatuck River closely matched those found in the Hammonasset River, with the concentrations of the Cu and Zn sulfide complexes being <3.5 nM. On the Quinnipiac River, higher concentrations of metal sulfide complexes were found at the upstream sampling site, which was located close to a headwater marsh system. This substantial increase in metal sulfide complexes between downstream and upstream sampling locations was attributed to the impact of treated sewage.

A comparison was made with the corresponding total Cu and Zn metal concentrations to estimate the percentage of dissolved metal bound to sulfides (Table 3). However, since the exact stoichiometry cannot be determined for Cu and Zn sulfide complexes in field samples, an average metal:sulfide ratio was used to determine the amount of Cu and Zn metal complexed by sulfides. The percent Zn bound is based on a equal mixture of 1:1 and 2:3 complexes, giving a Zn:S ratio of 0.83. For the percent Cu bound, a mixture of the 1:1 (40%) and 2:3 (60%) stoichiometries was used, giving a Cu:S ratio of 0.76. Both of these ratios were based on the metal:S ratio used in sulfide titrations here and in ref *7*.

In general, the proportion of Cu estimated to be bound to sulfides was greater than for Zn. In most cases the Cu sulfides accounted for over 30% of the dissolved metal. In the Pawcatuck River, where less total Cu is present, this ratio was over 50%. In general, a higher percentage of complexed metal was observed during the May sampling, probably reflecting higher sulfide production rates. For Zn, sulfides complexed <10% of the total metal. However, this was not unexpected due to the greater amount of total dissolved Zn present in the rivers.

For the pH levels at which voltammetric analyses were conducted on the field samples, any PbS dissociation would have been measured in the same sulfide pool as Zn sulfides. However, total Pb_{diss} concentrations were typically 10 times lower than sulfide concentrations being dissociated. Therefore, the maximum contribution Pb sulfides could have assuming all the Pb was complexed to S would be only 10%. While PbS dissociation may not affect the total amount of sulfides measured, PbS complexation can still have a dramatic effect on Pb speciation.

Size Fractionation. Ultrafiltration revealed that the size fractionation of Cu and Zn sulfide complexes was dependent on the proximity to the sources of the metal sulfide complexes. Samples collected at the downstream sites on both the Naugatuck and Quinnipiac Rivers in May had the largest fractions of the <3000 MW size metal sulfide complexes accounting for over 60% of the total metal sulfide complexes measured. At the headwater location on the Quinnipiac River, the levels of the <3000 MW size Zn and Cu sulfide complexes accounted for over 40% of the total metal sulfide complexes. In contrast, at the upstream location on the Naugatuck River, less than 30% of the total metal sulfide complexes were <3000 MW in size, but unlike the upstream location on the Quinnipiac River, this site was not directly downstream from any headwater marshes.

The presence of >3000 MW size metal sulfide complexes may be explained by organic growth on the surfaces of the metal sulfide clusters. Aqueous clusters had been observed during zinc sulfide formation in laboratory-prepared solutions (*19*). While these clusters are not themselves >3000 MW, they may provide a surface to which various organic groups can bind. Phenyl groups can be organically "capped"

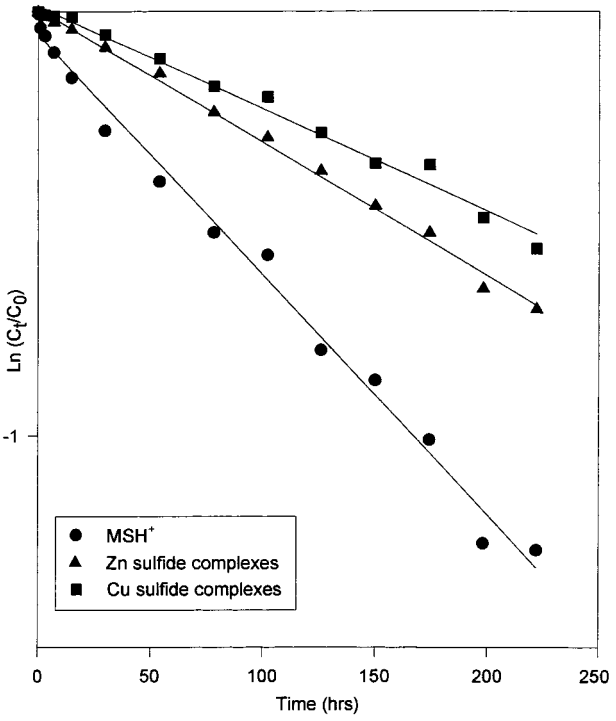

FIGURE 5. Metal sulfide oxidation kinetics in Naugatuck River water collected in May 1997. The slope of the graph represents a first-order oxidation rate constant k_{obs} (h^{-1}).

to the surface of CdSe clusters for laboratory purification (*20*). We hypothesize a similar mechanism may occur for metal sulfide complexes in natural waters. The addition of an organic layer may provide greater stability and account for the large fraction of >3000 MW size metal sulfide complexes that were observed. This could also explain why the metal sulfide complexes found in the Pawcatuck River (Table 3) are more resistant to dissociation at a lower pH than those created in laboratory-prepared solutions.

Alternatively, the >3000 MW metal sulfide complexes may be some type of an organic−sulfide−metal complex (R−S−Me). However, the reaction rates for metal sulfide formations are determined by the rate of water loss (k_{-w}), which is extremely fast for divalent cations. For the hexaquoiron-(II) complex, the log k_{-w} is 6−7, which gives rise to a k_f for $Fe(SH)^+$ of around 10^7 (*21*). Since, the water loss for the aquoions of Zn^{2+} ($k_{-w} = 3 \times 10^7$) and Cu^{2+} ($k_{-w} = 8 \times 10^8$) is faster (*22*), metal sulfide complexes would be predicted to react even more quickly, limiting the formation of any organic−sulfide−metal complexes.

First-Order Loss Kinetics. This research showed that metal sulfide complexes persist in oxic river water; however, little is known about the loss kinetics of these naturally occurring species.

In an effort to begin to understand the losses over longer time scales, the metal sulfide complexes in a sample of Naugatuck River (downstream sampling site) were monitored over a 10-day period in closed reaction vessels. The well-correlated regressions in Figure 5 indicate that first-order kinetics prevail. Assuming first-order kinetics, rate constants were calculated for each of the different metal sulfide complexes (Table 4). The calculated half-lives ranged from 5 to 21 days, with the Zn and Cu sulfide complexes having the greatest persistence. Our results are somewhat lower than those found by Vazquez et al. (*23*), who estimated the half-life of H_2S in surface ocean waters to be about 30 days based on kinetic experiments with Zn^{2+} and H_2S. One potential cause for the low half-lives is that a limited amount of organic matter was observed to have coagulated and precipitated during the course of the experiment. If metal sulfides were encased by organics, as proposed, precipitation would cause additional losses to the amount of metal sulfide complexes being measured. Unfortunately, the organic matter was not filtered and acidified to determine if sulfides had been trapped. Nevertheless, this experiment showed that metal sulfide complexes could be an important component of metal speciation on small- to medium-sized rivers with residences times on the order of a few weeks.

TABLE 4. First-Order Oxidation Rate Constants and Resulting Half-Lives for Metal Sulfides in Natural River Water

	rate constant (h^{-1})	half-life (days)
MHS^+	6.4×10^{-3}	6.5
Zn sulfides	2.5×10^{-3}	16.7
Cu sulfides	1.9×10^{-3}	21.9

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